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Adsorption Properties of Nitrogen, Carbon Dioxide and Nitrogen Dioxide onto Mesoporous Chromium Silicate

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Abstract. The adsorption properties of nitrogen, carbon dioxide and nitrogen dioxide onto mesoporous chromium silicates (Cr-FSM-16) were studied by spectroscopic analyses. The Cr-oxide moieties are highly dispersed in the framework of FSM-16. The UV-vis spectra of the Cr-FSM-16 exhibit three distinct absorption bands, which can be assigned to charge transfer from O^{2-} to Cr^{6+} of the tetrahedrally coordinated Cr-oxides moieties. The results of initial heat of adsorption of CO_2 indicated the interaction between $Cr^{6+}{=}\,O^{2-}$ in Cr-FSM-16 and CO_2 was weak. The decomposition of NO_2 by FSM-16 or Cr-FSM-16 was caused by Si—OH site or $Cr^{6+}{=}\,O^{2-}$ site, respectively. The co-adsorption models for NO_2 and CO_2 onto Cr-FSM-16 or FSM-16 were proposed in the end.

Keywords: adsorption, mesoporous chromium silicate, carbon dioxide, nitrogen dioxide

1. Introduction

Increasing attention has been paid to mesoporous materials with high surface area and narrow pore size distribution because of their diverse applications (e.g., adsorbents, catalysts, and host materials). FSM-16 (a folded-sheet mesoporous material) (Inagaki et al., 1993) and MCM-41 (Kresge et al., 1992) are typical examples of such materials.

Highly dispersed transition metal oxides incorporated within the framework of zeolites and mesoporous silicas provide unique reactivities not only for catalytic reactions but also for photocatalytic reactions (Buchel et al., 1998; Grün et al., 1999). In particular, high-dispersed transition metal oxides such as titanium, vanadium and molybdenum exhibit high photocatalytic reactivities for various reactions. However, photo catalysts containing these metal oxides are efficient only under UV light irradiation and exhibit no photocatalytic reactivity under visible light irradiation. In order to establish the clean photo catalysis system using the most environmentally ideal energy source-solar light, it is vital to develop a photocatalyst that can operate efficiently under visible light irradiation. Cr-containing mesoporous silicas (Cr-HMS) in which tetrahedrally isolated chromium oxide (chromate) moieties coordinated are effective photo catalysts for the decomposition of NO and the partial oxidation of propane with molecular oxygen under visible light irradiation (Yamashita et al., 2001).

The adsorption on photo catalysts, in particular, the adsorption of carbon dioxide, cannot be neglected for the practical using of photo catalysts. In addition, the interaction between NOx and adsorbed carbon dioxide on photo catalysts also cannot be neglected. But there have been few reports on the adsorption properties of mesoporous chromium silicate. One of the authors has studied the adsorption of NOx on micro porous material (ZSM-5) (Katoh et al., 1995), carbon dioxide on ZSM-5 (Yamazaki et al., 1993) and meso porous material (FSM-16) (Katoh et al., 2000). The adsorption properties were examined by IR spectroscopy.

In the present study, chromium-containing mesoporous silicas (Cr-FSM-16; BET surface area: ca. 600 m^2/g, pore size: ca. 2.8 nm) have been prepared and characterized by XRD, XRF and UV-vis. These

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obtained results and the reported results (the initial heat of adsorption and IR spectra) (Katoh et al., 2004) were discussed. On the basis of these data, the co-adsorption models for NO_2 and CO_2 onto Cr-FSM-16 and FSM-16 were proposed in the end.

2. Materials and Methods

2.1. Materials

Cr-FSM-16 crystals were prepared using sodium silicate and chromium (III) nitrate as the starting materials and hexadecyl-trimethyl-ammonium chloride as a template with preparation conditions combining those reported by Inagaki et al. (1993) and Naono et al. (1997). The pH suspension was adjusted to 8.5 by addition of 2 moldm^{-3} HCl solution and the suspension was left for a further 9 h at 343 K and filtrated. The white precipitate was calcined at 823 K in a stream of nitrogen for 6 h, followed in a stream of air for 2 h. Through this process, the surfactant was removed from the precipitate.

2.2. Methods

The XRD patterns were recorded on a Rigaku diffractometer (RINT2500-VHF) using a radiation of Cu-Kα (100 mA, 30 kV). The content of Cr in Cr-FSM-16 was measured by XRF (EDX-700/800, SHIMADZU). The powders were characterized by UV-vis spectrophotometer (SHIMADZU 2500PC) with an integrating sphere attachment ISR 2200 for their diffuse reflectance in the range of 200 to 800 nm. $BaSO_4$ was used as the standard in these measurements.

3. Results

3.1. Cr Content and XRD Patterns for Cr-FSM-16

Figure 1 shows the XRD patterns of FSM-16 and Cr-FSM-16 [x] (denote the ratio of Si/Cr). Cr-FSM-16 had a Characteristic peak around $2\theta = 2$–3deg. The peak positions for Cr-FSM-16 [110] and [170] were lower than that for FSM-16. This means they maintain mesoporous structures and that the Cr-oxide moieties are highly dispersed in the framework of FSM-16 (Zhang et al., 1996). While, the peak position for Cr-FSM-16 [100] was higher than that for FSM-16. For Cr-FSM-16 [100], highly dispersed Cr-oxide moieties could not be confirmed by XRD.

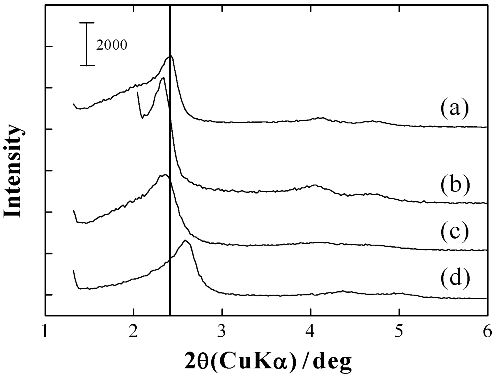


Figure 1. Powder X-ray diffraction patterns for FSM-16 (a), Cr-FSM-16 [110] (b), [170] (c) and [100] (d).

Figure 2 shows the Si/Cr ratio for starting materials (reactants) and prepared Cr-FSM-16 (products). The ratio for reactants was almost proportional to the ratio for products. Circles denote the Cr-FSM-16 has Cr-oxide moieties dispersed in the framework, while triangles denote their state of Cr-oxide could not be confirmed by XRD. So, only Cr-FSM-16 having tetrahedral Cr-oxide in the framework was discussed below.

3.2. UV-Vis Spectra of Cr-FSM-16

Figure 3 shows UV-spectra of Cr-FSM-16 and FSM-16. The UV-vis spectra of the Cr-FSM-16 exhibited three distinct absorption bands at around 270, 360 and

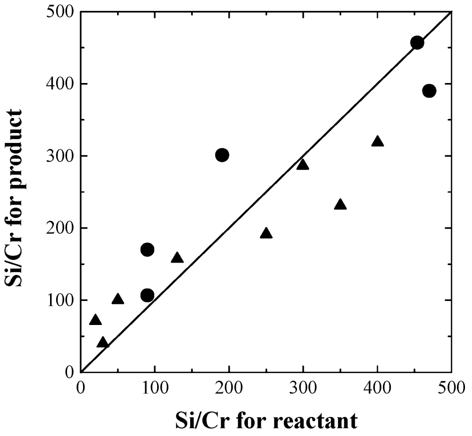


Figure 2. Si/Cr for reactant vs. for product; (●) Cr-oxide moieties was dispersed in the framework of FSM-16, (▲) Cr-oxide moieties dispersed in the framework of FSM-16 could not be confirmed by XRD.

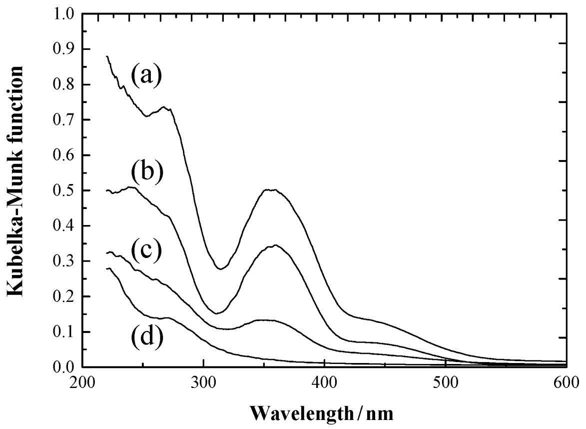


Figure 3. UV-spectra of Cr-FSM-16 [170] (a), [110] (b), [300] (c) and FSM-16 (d).

460nm, which could be assigned to charge transfer from O^{2-} to Cr^{6+} of the tetrahedrally coordinated Cr-oxide moieties (Weckhuysen et al., 1994). These absorption bands at 270 and 360 nm were assigned to $^1A_1 \rightarrow {}^1T_2$ transition of tetrahedral Cr-oxide. The band at 460 nm was assigned to the symmetry-forbidden nature of the $^1A_1 \rightarrow {}^1T_1$ transition of tetrahedral Cr-oxide (Iannibello et al., 1984). Without Cr ion, the spectra of FSM-16 exhibited only absorption band around 270 nm above 220 nm. The absorption bands assigned to the absorption of dichromate or Cr_2O_3 cluster could not be observed above 550 nm, indicating that tetrahedrally coordinated Cr-oxide species existed in an isolated state.

4. Discussion

4.1. Initial Heat of Adsorption of N_2 or CO_2 on Cr-FSM-16

Table 1 shows the initial heat of adsorption of N_2 or CO_2 onto FSM-16 or Cr-FSM-16 [170] (Katoh et al., 2004). The values for N_2 and CO_2 were calculated by using the Clausius-Clapeyron equation and their adsorption isotherms at the temperature region 200 K–243 K and 273 K–423 K, respectively. The value for CO_2 adsorption on FSM-16, a typical example of meso porous silicates, was higher than the value for N_2 adsorption on that. Additionally, the value of N_2 or CO_2 onto silicalite, a typical example of micro porous silicates, was 16.2 kJ/mol (Yamazaki et al., 1988) and 23.4 kJ/mol (Yamazaki et al., 1993), respectively. These results indicate that CO_2 interacts strongly with meso or micro porous silicates. In particular, surface free SiOH groups of FSM-16 were interacted strongly with CO_2 (Katoh et al., 2000). But the value for CO_2 adsorption on Cr-FSM-16 [170] was lower than the value for N_2 adsorption on that. So, the origin of low value for CO_2 on Cr-FSM-16 was the interaction between Cr and CO_2. That is to say, the interaction between the adsorption sites formed by Cr^{6+}—O^{2-} and CO_2 was weak.

Table 1. Initial heat of adsorption (kJ/mol) of N_2 or CO_2 onto FSM-16 or Cr-FSM-16 [170].

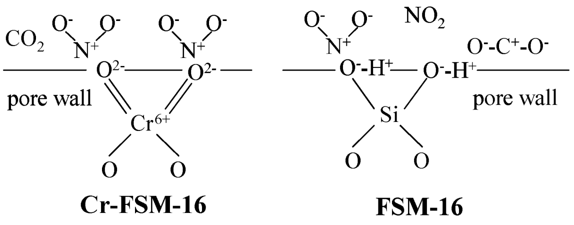
Adsorbent	N_2	CO_2
FSM-16	12.0	21.6
Cr-FSM-16 [170]	16.3	10.5

4.2. IR Spectra of NOx Adsorbed on Cr-FSM-16

When NO_2 was adsorbed onto FSM-16 or Cr-FSM-16 at 303 K under no light, not only the adsorbed NO_2 but also absorption bands of NO and N_2O_3 adsorbed were measured by IR spectroscopy (Katoh et al., 2004). These results indicate that (1) NO_2 decomposed to NO on FSM-16 or Cr-FSM-16 and (2) NO and NO_2 formed N_2O_3. This decomposition of NO_2 by FSM-16 and Cr-FSM-16 was caused by SiOH and Cr^{6+}—O^{2-}, respectively. Additionally, NO_2 decomposition on Cr-FSM-16 was affected by co-adsorbed CO_2, but the degree of effect on Cr-FSM-16 was lesser than that on FSM-16.

4.3. Co-Adsorption models for NO_2 and CO_2 onto Cr-FSM-16 or FSM-16

The co-adsorption models for NO_2 and CO_2 onto Cr-FSM-16 or FSM-16 were proposed on the base of the above data (Scheme 1). For Cr-FSM-16, NO_2 selectively adsorbed on Cr^{6+}=O^{2-} site, because the



Scheme 1. Co-adsorption models for NO_2 and CO_2 onto Cr-FSM-16 or FSM-16.

interaction between $Cr^{6+}{=}O^{2-}$ and CO_2 was weak. N^+ of NO_2 would interact with O^{2-} of $Cr^{6+}{=}O^{2-}$, and then NO_2 would be decomposed to NO by the site. While, for FSM-16, both NO_2 and CO_2 was adsorbed onto Si—OH site. N^+ of NO_2 would interact with O^- of Si—OH, and O^- of CO_2 would interact with H^+ of Si—OH. The amount of adsorbed NO_2 decreased and the decomposition was affected by co-adsorbed CO_2. As the conclusion, Cr-FSM-16 has advantage of NO_2 decomposition under CO_2 atmosphere relative to FSM-16.

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